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OPTICAL AND PHOTOVOLTAIC PROPERTIES OF CuSe THIN FILMS

U. J. Chavan [1] | Abhijit A. Yadav [1]

[1] Thin Film Physics Laboratory, Department of Physics, Electronics and Photonics, Rajarshi Shahu Mahavidyalaya, Latur, (M.S.) 413512 India

ABSTRACT

Copper selenide thin films have been deposited by spraying a mixture of aqueous solutions (0.50 M) of copper chloride hydrate (CuCl2·2H2O) and selenourea (H2NC (Se) NH2) at various substrate temperatures. The as deposited copper selenide thin films were used to study a wide range of characteristics including structural, surface morphological, optical, electrical, and photovoltaic power output characteristics. X-ray diffraction (XRD) study reveals that the films are polycrystalline in nature with hexagonal (mineral klockmannite) crystal structure. The SEM study reveals that the grains are uniform with uneven spherically shaped and spread over the entire surface of the substrates. The direct band gap values are found to be in the range 2.29-2.36 eV depending on the substrate temperature. The measured values of efficiency (η) and fill factor (FF) are found to be 0.99 % and 0.51 respectively for film deposited at 350°C.

KEY WORDS: thin films; chemical synthesis; electrical characterization; crystal structure.

INTRODUCTION

Currently; much importance has been given to study the deposition and characterization of semiconducting metal chalcogenide and chalcopyrite thin films because of their various optoelectronic properties and applications. There are considerable interests in the field of solar selective coating, optoelectronic devices, electronics and electrical devices [1-7]. Copper selenide is a p-type semiconductor material due to copper vacancies; that has suitable electrical and optical properties for a number of applications in solar cells, super ionic conductors and photo-detectors, etc. The indirect band gap of 1.1-1.27eV makes this material an absorbent material and a direct band gap > 2eV, makes it a window layer material in solar cells [8, 9].

Various methods so far adopted for the preparation of copper chalcopyrite thin films include chemical bath deposition [10], selenization [11, 12] sputtering [13], electrochemical deposition [14], galvanic synthesis [15], co-deposition [16], evaporation [17], electrodeposition [18, 19], solvothermal method [20], MOCVD [21] and spray pyrolysis technique etc. A very few reports are available on synthesis of copper selenide by spray pyrolysis. The spray pyrolysis method presents some noticeable advantages, such as: a wide possibility of varying the film properties by changing the composition of the starting solution (introduction of dopants and change the film microstructure) and low cost when large-scale production is needed. Since the study of optical and electrical analysis plays an important role in device fabrication (Opto-electronic devices). Keeping in view all these aspects an attempt has been made to deposit copper selenide thin films at various substrate temperatures and additionally its effect on optical, compositional, electrical and photoelectrochemical properties has been studied.

EXPERIMENTAL DETAILS

Copper selenide thin films were deposited onto glass substrates by a spray pyrolysis method at 300 to 400°C substrate temperatures at the interval of 25°C. Aqueous solutions (0.050M) of copper chloride hydrate ($CuCl_2 \cdot 2H_2O$) and selenourea ($H_2NC(Se)NH_2$) were utilized as starting materials. Glass microslides of the size 7.5 × 2.5 cm^2 and FTO coated glass were used as substrates. The temperature of substrate was controlled by an iron–constantan thermocouple. A spray rate of 4mlmin^{-1} was kept constant throughout the experiment. The distance between the nozzle and the substrate was 28 cm. The as deposited thin films of copper selenide were characterized for structural, morphological, compositional, optical, electrical, photoelectrochemical measurements.

RESULTS AND DISCUSSION

STRUCTURAL ANALYSIS

The crystal structure of copper selenide thin films was studied by X-ray diffraction with Cu-K_α radiation (1.5406 Å). The range of 2θ angle was from 10 to 80°. Fig. 1 shows typical X-ray diffractogram of copper selenide film deposited at 350°C. X-ray diffraction patterns reveal that the films of copper selenide deposited by spray pyrolysis technique are polycrystalline in nature. It was observed that the high intensity reflection peaks at 2θ = 31.10° (006) plane, 2θ = 26.18° (101) plane, 2θ = 28.02° (102) and plane 2θ = 66.46° (207) plane for CuSe thin film. A comparison of observed and the standard 'd' values for (h k l) planes ensures that copper selenide shows hexagonal (mineral klockmannite) crystal structure irrespective of substrate temperature [22]. Additionally peaks corresponding to Cu_3Se_2 (Tetragonal) [23] were also detected with less intensity. Although, there are more than eight stoichiometries of copper selenide, and some stoichiometries have different phases each of them has their own characteristic X-ray diffraction pattern [24]. Therefore, the X ray diffraction patterns give the most positive evidence of the formation of CuSe phase, which was desired. After refinement, the cell constants were calculated to be a = b = 3.969Å and c = 17.059Å; which are consistent with the reported data [23].

Crystallite size was estimated by using Scherrer's formula given by the equation,

$$D = \frac{k\lambda}{\beta \cdot \cos\theta} \qquad (1)$$

where k varies from 0.89 to 1.39. But in most of the cases it is closer to 1. Hence for grain size calculation it is taken to be one, λ is wavelength of X-ray, β is the full width at half of the peak maximum in radians and θ is Bragg's angle. The crystallite size was estimated for the standard (006) reflection. The crystallite size for copper selenide thin films was found to be in the range of 23-28 nm.

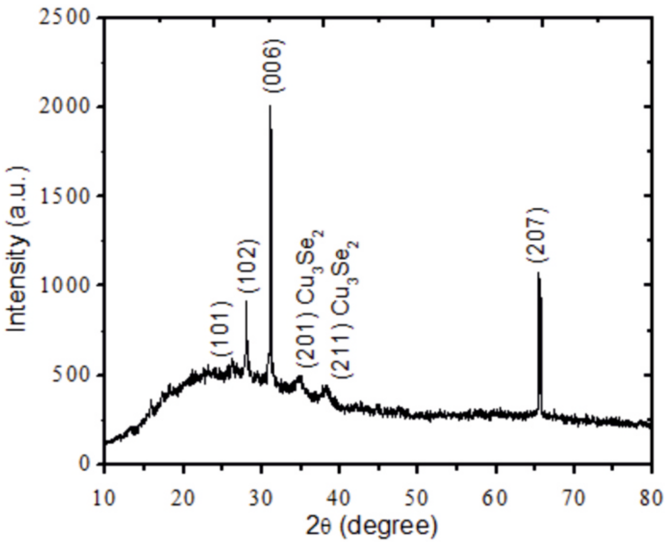

Fig.1 X-ray Diffraction pattern of CuSe thin film at a substrate temperature of 350°C.

OPTICAL ANALYSIS

The optical band gap energy E_g can be ascertained from the experimental values of absorption coefficient α as a function of photon energy hυ, using the following relation

$$\alpha h\nu = A\left(h\nu - E_g\right)^n \qquad (2)$$

Where A is the constant, E_g is the band gap energy, hυ is the photon energy, n= ½ or 2 for direct or indirect transition. The value of absorption coefficient is found to be of the order of 10^4 cm^{-1}. The plot of $(\alpha h\upsilon)^2$vs (hυ) is shown in Fig. 3 which is linear at the absorption edge, indicating a direct allowed transitions. The straight line portion was extrapolated to the energy axis and when $(\alpha h\upsilon)^2 = 0$, the intercept gives the band gap energy of CuSe. The band gap energy is found to be 2.29 eV for film deposited at 350ºC comparable with values reported earlier [8, 25].It was observed that with the variation of substrate temperature, band gap energy E_g decreases reaches a minimum value 2.29 eV at 350ºC and further increases with increase in substrate temperature.

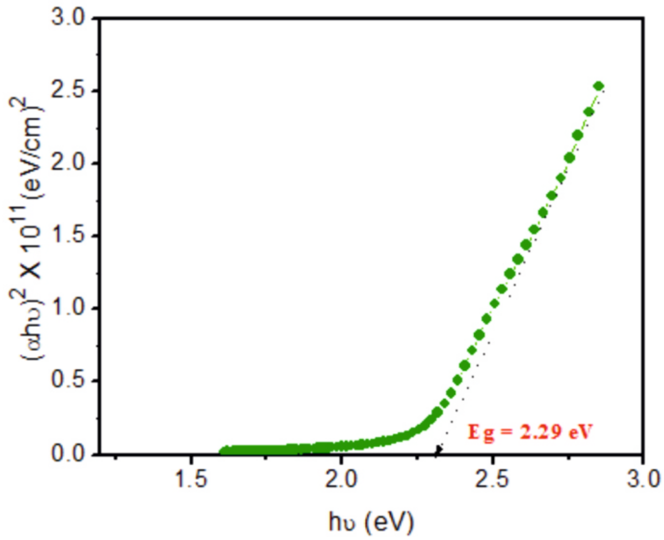

Fig. 2 Variation of $(\alpha h\nu)^2$ versus hν of copper selenide thin film at a substrate temperature of 350°C

PHOTOVOLTAIC POWER OUTPUT STUDIES

This technique is used to determine the properties of semiconductor/electrolyte interface involve the illumination of the interface with a light of suitable wavelength that shows photovoltaic effect. The photovoltaic output characteristics were examined under a light intensity of 25mWcm^{-2} for films deposited at all substrate temperatures. Typical photocurrent density versus photo voltage characteristics of spray deposited p-copper selenide films/K_2SO_4 interface deposited at 350°C under illumination is shown in Fig.3.

The maximum power conversion efficiency (η) is found to be 0.99 % for copper selenide thin film deposited on FTO coated glass substrate at a substrate temperature of 350°C, while it was less for other substrate temperatures. This efficiency is comparable with results reported by Kozytskiy et al. [26]. Though the obtained conversion efficiency is less, there is a scope for the improvement of the efficiency. The series and shunt resistances are found to be 238 Ω and 1.736 kΩ from the slope of the power characteristic at I = 0 and V = 0, respectively. The micro crystallites are in general normal to the film plane, which makes leakage of current across the semiconductor surface [27]. Ideally, the shunt resistance should be infinite, so that at that place will not be leakage current.

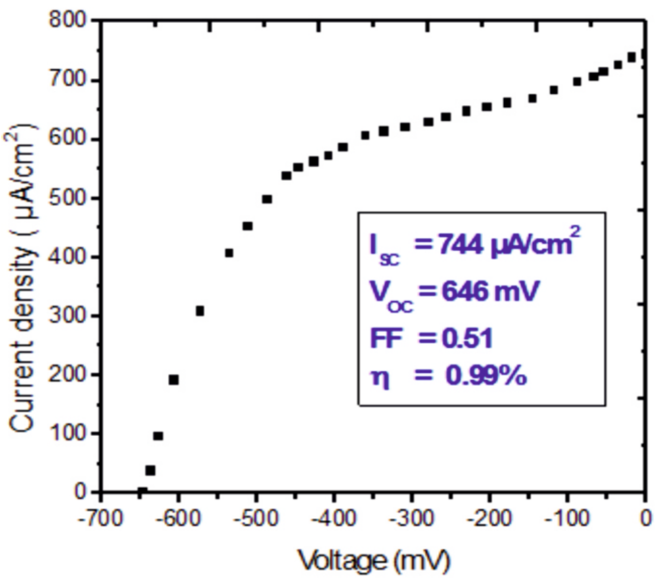

Fig. 3 Plot of power output characteristics of copper selenide thin films deposited at a substrate temperature of 350°C.

CONCLUSIONS

Copper selenide thin films have been successfully deposited using the simple and inexpensive spray pyrolysis technique. XRD study revealedthe polycrystalline nature of the films with hexagonal (mineral klockmannite) crystal structure irrespective to substrate temperatures. Scanning electron microscopy studies reveal uniform deposition with the average grain size of 85 nm. The optical absorption study revealed direct band gap nature with the band gap energy in the range 2.29-2.36 eV. The conversion efficiency (η) and fill factor (FF) for p-copper selenide/0.5M K_2SO_4/C PEC cell configuration are found to be 0.99% and 0.51 respectively for film deposited at 350°C, as the deposited films have high series resistance.

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